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MAGNETISM
AND FERROELECTRICITY

Electron Paramagnetic Resonance of Ce^{3+} and Nd^{3+} Impurity Ions in $YBa_2Cu_3O_{6.13}$

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Abstract—The electron paramagnetic resonance (EPR) spectra of Ce^{3+} and Nd^{3+} impurity ions in unoriented powders of the $YBa_2Cu_3O_{6.13}$ compound are observed and interpreted for the first time. It is demonstrated that, upon long-term storage of the samples at room temperature, the EPR signals of these ions are masked by the spectral line (with the g factor of approximately 2) associated with the intrinsic magnetic centers due to the significant increase in its intensity.

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1. INTRODUCTION

Among the large family of copper-containing high-temperature oxide superconductors, the $YBa_2Cu_3O_x$ (Y–Ba–Cu–O) compound with structural and physical properties dependent on the oxygen index $6 \le x \le 7$ has been investigated especially extensively, including electron paramagnetic resonance (EPR) studies. In particular, this is favored by the fact that the replacement of yttrium (which is located between two superconducting planes CuO_2) by other rare-earth ions (except for praseodymium, cerium, and terbium) at any concentrations almost does not affect the superconducting properties of the material [1]. The majority of EPR investigations have been performed with the use of samples doped with trivalent gadolinium (Gd^{3+}) ions. This has made it possible to obtain important information on the types and magnitudes of interactions directly in the bulk of the material. However, the bibliography of EPR experiments with impurities of other rare-earth ions is rather limited (see, for example, [2–9]). It is interesting that EPR signals have been reliably observed only from ions of the right half of the rare-earth series (erbium, ytterbium, dysprosium, terbium), whereas a few attempts to detect the EPR absorption for some ions of the left half of this series (neodymium, praseodymium, samarium) seem to be inconclusive. For example, information on the observation of the Pr^{4+} EPR signal in the Y–Ba–Cu–O compound [10] is most likely erroneous because this signal should be characterized by a strong anisotropy of the g factor with values substantially different from $g \approx 2$, should have a larger hyperfine interaction constant, and cannot be detected at room temperature.

Moreover, it should be noted that the results of EPR experiments for the Y–Ba–Cu–O compound sometimes do not correlate with each other, which is associated with the problems of the preparation of perfect crystals, the control for the doping level, the homogeneity of samples, their ageing, etc. In this respect, it is important to compare the experimental results obtained for samples prepared using different techniques and to analyze variations with time.

The aforesaid is especially true in regard to the interpretation of the EPR spectra of *intrinsic magnetic centers* in the Y–Ba–Cu–O compound, which frequently leads to very contradictory results. Immediately after the discovery of superconductivity in the Y–Ba–Cu–O compound, numerous experiments (see the review [11] and the corresponding references therein) revealed the EPR signal typical of Cu^{2+} ions with the axial symmetry ($g_\parallel \approx 2.20$, $g_\perp \approx 2.05$) characterized by an insignificant orthorhombic distortion. In the majority of earlier works, the observed signals were associated with the presence of impurity phases CuO, $BaCuO_2$, $Y_2Cu_2O_5$ (blue phase), and Y_2BaCuO_5 (green phase). Therefore, the EPR signal at $g \approx 2$ was treated as an indication of the degree of purity of the sample and attributed to Cu^{2+} ions located at the Cu(1) position [12]. With an improvement of the technique used for preparing samples, it has become clear that no EPR signals are observed in the "pure" $YBa_2Cu_3O_7$ compound. In order to explain this fact, several assumptions have been made [11, 12]. For example, the antiferromagnetic

interaction leads to the formation of Cu^{2+} pairs for which the nonmagnetic singlet ($S = 0$) is the ground state and the triplet ($S = 1$) is the excited state. The wide energy spacing between the ground and excited states does not enable one to observe the EPR signal for the triplet components. At present, reasoning from the results of experiments with La_2CuO_{4+x} compounds, it has been universally accepted that the impossibility of observing the Cu^{2+} EPR signal in quasi-two-dimensional cuprate high-temperature superconductors is explained by the large line width due to the static and dynamic components of the antisymmetric part of the Dzyaloshinskii–Moriya exchange interaction [11].

The purpose of the present work was to investigate the possibility of using localized magnetic moments of cerium and neodymium rare-earth elements as an impurity paramagnetic probe for the study of normal and superconducting properties of the Y–Ba–Cu–O compound with the use of EPR spectroscopy.

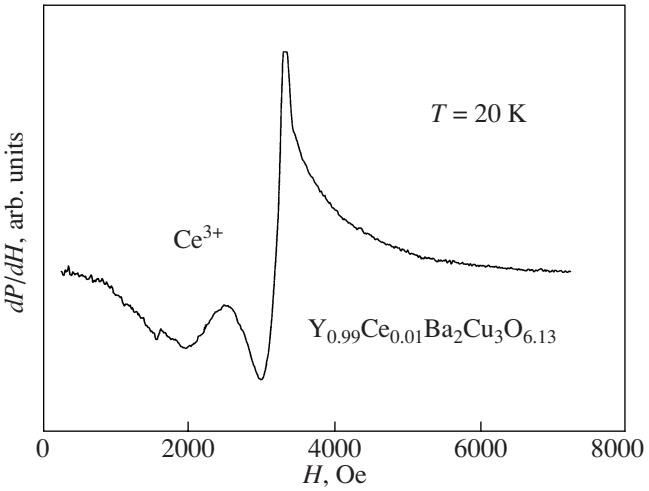

Fig. 1. EPR spectrum of the $Y_{0.99}Ce_{0.01}Ba_2Cu_3O_{6.13}$ compound at $T = 20$ K (within three weeks after the preparation of the sample).

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Oxygen-deficient samples $Y_{0.99}Ce_{0.01}Ba_2Cu_3O_x$ and $Y_{0.99}Nd_{0.01}Ba_2Cu_3O_x$ were prepared using conventional solid-phase synthesis from the initial components Y_2O_3, CeO_2 (or, correspondingly, Nd_2O_3), $BaCO_3$, and CuO (Alfa, 99.99%). The corresponding amounts of the initial reactants were mixed in an agate mortar, and the prepared mixture was used for synthesizing the samples in air at temperatures of 800–920°C for at least 150 h with several intermediate grindings. Then, the samples were enriched in oxygen at a temperature of 500°C for several hours (at an oxygen pressure of 1 atm), followed by slow cooling. After this procedure, the oxygen content was equal to 6.98. The samples with the required oxygen content were produced by their heating with the appropriate amount of metallic copper in evacuated sealed silica tubes (850°C; 10 h; cooling rate, 10°C/h). The oxygen content in the reduced samples was controlled by comparing the calculated and measured changes in the weights of oxidized copper and the reduced sample and amounted to ~6.13 for all samples. It is this oxygen concentration that corresponds to the lowest intensity of the EPR signal at $g \approx 2$, which can substantially complicate the possible recording of the EPR spectra of rare-earth ions. The phase purity of the initial and reduced samples was confirmed by X-ray diffraction analysis on a Siemens D500 diffractometer. The EPR spectra were measured on a Bruker ESP-300 spectrometer at a frequency of ~9.4 GHz in the temperature range 5–35 K.

In order to reveal the Ce^{3+} and Nd^{3+} EPR signals, we investigated the $Y_{0.99}Ce_{0.01}Ba_2Cu_3O_{6.13}$ and $Y_{0.99}Nd_{0.01}Ba_2Cu_3O_{6.13}$ compounds in the form of powders mixed with a paraffin. The investigations were performed three times with an interval of three months. For convenience of comparison of the EPR line intensities, we used the reference sample of the composition CaF_2 + 0.8% Er^{3+} with cubic centers characterized by the EPR line at $g = 6.785$ with the width comparable in the order of magnitude to the line width of the compounds under investigation.

3. RESULTS AND DISCUSSION

3.1. EPR Spectra of the $Y_{0.99}Ce_{0.01}Ba_2Cu_3O_{6.13}$ Compound

The first attempt to detect the EPR spectrum of the $Y_{0.99}Ce_{0.01}Ba_2Cu_3O_{6.13}$ compound was made within three weeks after the preparation of the sample. It was revealed that the EPR spectrum is observed at temperatures below 25 K and consists of two signals (Fig. 1). The more intense EPR signal at $g \approx 2$ (i.e., with the resonance field $H_{res} \approx 3212$ Oe) is characteristic of oxygen-deficient undoped samples Y–Ba–Cu–O [11, 12]. The other EPR signal at $g \approx 3.01$ ($H_{res} \approx 2255$ Oe) is well resolved in the temperature range $10 \text{ K} < T < 20$ K and is saturated at lower temperatures. It is reasonable to assign this signal to the Ce^{3+} ions. Actually, this behavior is typical of the Ce^{3+} EPR spectrum, which, as a rule, is not observed at temperatures above 30 K due to the fast spin–lattice relaxation [13]. Only at temperatures $T \leq 20$ K, the spin–lattice relaxation times of Ce^{3+} ions are long enough for the EPR spectrum to be recorded. The factor $g = 3.01$ determined from these experiments is in reasonable agreement with the theoretical estimates made in [14] for the g factors of the Ce^{3+} ion in the Y–Ba–Cu–O compound: $g_x \approx 0.496$, $g_y \approx 0.431$, and $g_z \approx 3.971$ (in the case where the observed EPR spectrum is associated with the g_z component). Our corresponding calculations of the g factors with the use of the crystal field parameters for the

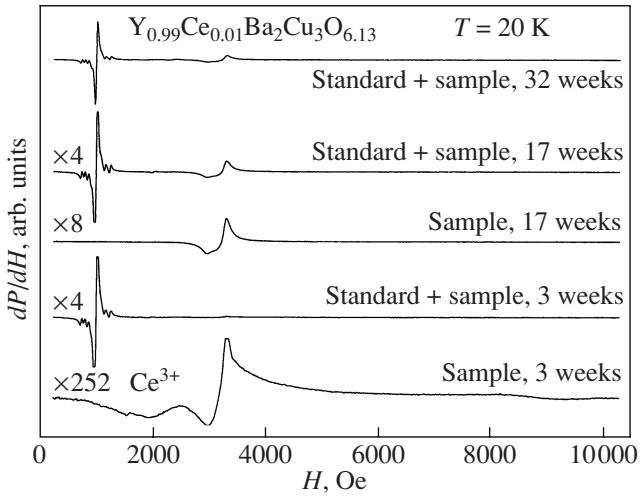

Fig. 2. EPR spectra of the $Y_{0.99}Ce_{0.01}Ba_2Cu_3O_{6.13}$ compound with an impurity of 1% Ce^{3+} at $T = 20$ K for different instants of time (within 3, 17, and 32 weeks after the preparation of the sample).

Nd^{3+} ion in the $NdBa_2Cu_3O_{6.0}$ compound led to close values [15]: $g_x = -1.246$, $g_y = -1.246$, and $g_z = 3.462$.

Long-term storage of the sample at room temperature results in substantial changes in the EPR spectrum. Beginning with the second series of the EPR experiments performed within three months after the first experiments, we observed a sharp increase in the intensity of the signal at $g \approx 2$ and a distortion of the EPR line shape, which was accompanied by masking (suppressing) the signal from the Ce^{3+} ions (Fig. 2). It should be noted that, in the study of the Y–Ba–Cu–O compound with a low oxygen content and the Gd^{3+} impurity, Rockenbauer et al. [16] observed a similar time evolution of the portion of the EPR spectrum at $g \approx 2$, which was attributed to the copper ions.

In order to determine the concentration of magnetic centers associated with the Ce^{3+} ions and the signal at $g \approx 2$ in the sample, we evaluated the ratios of the areas of these signals with respect to the reference sample (the concentration of magnetic centers in the reference sample is equal to 1.2×10^{18} spins). The results obtained were used to estimate the concentration of Ce^{3+} centers per cubic centimeter and to determine the percentage ratios of the signal at $g \approx 2$ with respect to the number of Cu(1) atoms and the signal from the rare-earth ions with respect to Y^{3+} ions. The results of calculations are listed in the table. A considerable deviation (by a factor of almost five) of the measured concentration of Nd^{3+} impurity ions (from a concentration of 1% specified in the synthesis of the sample) is primarily explained by the impossibility of determining all components of the g tensor from our EPR experiments, in which we studied unoriented polycrystals rather than single crystals. That is why the observed EPR spectrum cannot be interpreted with due regard for all paramagnetic impurity centers contained in the sample.

3.2. EPR Spectra of the $Y_{0.99}Nd_{0.01}Ba_2Cu_3O_{6.13}$ Compound

Compounds Y–Ba–Cu–O containing small additives of neodymium have never been investigated by the EPR method. There are only several works devoted to the study of Y–Ba–Cu–O compounds by EPR spectroscopy in which the Y^{3+} ions were either completely or 50% replaced by the Nd^{3+} ions [17–19]. Guskos et al. [17] investigated the Nd–Ba–Cu–O compound with a low oxygen content (not a superconductor) at $T \approx 77$ K and observed two lines: a narrow line (with the width $\Delta H_{pp} \approx 150$ Oe at $g = 3.6$) and a broad line (with the width $\Delta H_{pp} \approx 1000$ Oe at $g \approx 2.13$). In the authors' opinion, these lines are associated with the Nd^{3+} ions. However, it is known that Nd^{3+} EPR signals have never been observed at the liquid-nitrogen temperature due to the fast spin–lattice relaxation [13]. At least the narrow signal at $g = 3.6$ can in no way be attributed to the Nd^{3+} ions. According to Likodimos et al. [18], who studied the $Y_{0.5}Nd_{0.5}Ba_2Cu_3O_x$ compound by the EPR method at lower temperatures (3–70 K), Nd^{3+} EPR signals are not observed as a result of fast spin–lattice relaxation. This also seems to be highly improbable because it is well known that, at $T < 20$ K, the relaxation times of the Nd^{3+} ions are sufficiently long and EPR signals can be

Main characteristics of the signals in the EPR spectra of the $Y_{0.99}Ce_{0.01}Ba_2Cu_3O_{6.13}$ and $Y_{0.99}Nd_{0.01}Ba_2Cu_3O_{6.13}$ compounds and their variation with time

Time of the experiment (number of weeks after the preparation of the sample)	Concentration of magnetic centers of the signal at $g \approx 2$ in $Y_{0.99}Ce_{0.01}Ba_2Cu_3O_{6.13}$ (spins/cm^3)	Ratio of magnetic centers of the signal at $g \approx 2$ to Cu(1) ions in $Y_{0.99}Ce_{0.01}Ba_2Cu_3O_{6.13}$ (%)	Concentration of magnetic centers of the signal at $g \approx 2$ in $Y_{0.99}Nd_{0.01}Ba_2Cu_3O_{6.13}$ (spins/cm^3)	Ratio of magnetic centers of the signal a $g \approx 2$ to Cu(1) ions in $Y_{0.99}Nd_{0.01}Ba_2Cu_3O_{6.13}$ (%)	Ratio of magnetic centers of the signal from Ce^{3+} and Nd^{3+} ions to Y^{3+} ions (%)
3	3.74×10^{19}	0.65	3.60×10^{19}	0.63	0.23(Ce^{3+}) 0.13(Nd^{3+})
17	5.24×10^{20}	9	7.05×10^{20}	12.2	–
32	7.50×10^{20}	13	5.03×10^{20}	8.7	–

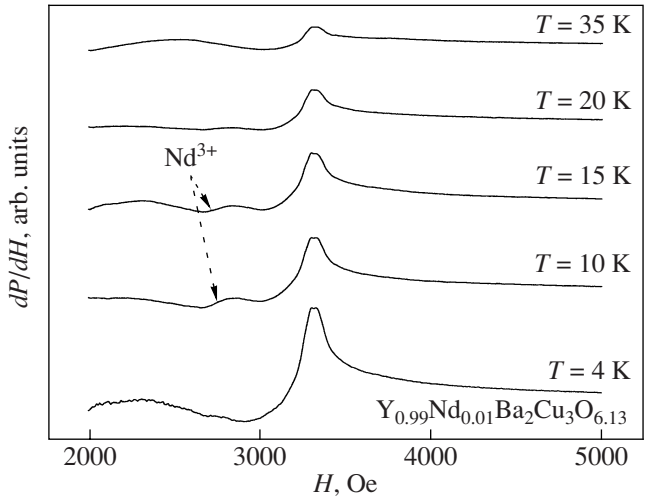

Fig. 3. Temperature dependence of the EPR spectrum of the $Y_{0.99}Nd_{0.01}Ba_2Cu_3O_{6.13}$ compound within three weeks after the preparation of the sample.

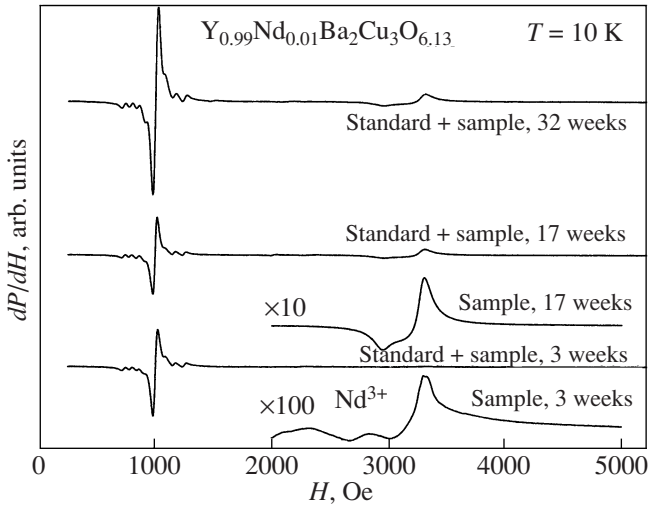

Fig. 4. EPR spectra of the $Y_{0.99}Nd_{0.01}Ba_2Cu_3O_{6.13}$ compound with an impurity of 1% Nd^{3+} at $T = 10$ K for different instants of time (within 3, 17, and 32 weeks after the preparation of the sample).

detected easily. Baranov et al. [19] investigated Nd–Ba–Cu–O ceramic materials and single crystals in the temperature range 4–300 K at frequencies of 9.3 and 35 GHz. The authors observed the intense broad EPR lines at $T < 40$ K ($g_\parallel \approx 2.15$, $g_\perp \approx 2.2$ at 10 K) and assigned them to the Cu^{2+} ions rather than to Nd^{3+} ions. Therefore, the analysis of the results obtained in the above works demonstrates that no Nd^{3+} EPR signals were detected in the Y–Ba–Cu–O compound.

With the aim of revealing the Nd^{3+} EPR signals, we studied the $Y_{0.99}Nd_{0.01}Ba_2Cu_3O_{6.13}$ compound. The EPR spectrum assigned to the Nd^{3+} ions (Fig. 3) is reliably observed in the resonance field $H_{res} \approx 2760$ Oe at temperatures in the range 10 K $< T <$ 20 K. The probable saturation of this signal complicates its detection with a further decrease in the temperature. In turn, at $T > 20$ K, the EPR spectrum is not observed as a result of relaxation broadening. Long-term storage of the sample at room temperature results in substantial changes in the EPR spectrum. As for the $Y_{0.99}Ce_{0.01}Ba_2Cu_3O_{6.13}$ compound, beginning with the second series of the EPR experiments (i.e., within 17 weeks after the preparation of the sample), we observed a considerable increase in the intensity of the signal at $g \approx 2$, which leads to the suppression of the signal from the Nd^{3+} ions (Fig. 4).

The estimates of the concentration of magnetic centers associated with the Nd^{3+} ions per cubic centimeter and the percentage ratios of the signal at $g \approx 2$ with respect to the number of Cu(1) atoms and the signal from these rare-earth ions with respect to Y^{3+} ions are presented in the table. The experimental g factor for the Nd^{3+} ion is estimated to be $g \approx 2.45$, which is in reasonable agreement with our calculations for the Y–Ba–Cu–O compound containing the Nd^{3+} impurity with the use of the crystal field parameters for the Nd^{3+} ion in the $NdBa_2Cu_3O_{6.0}$ compound [15]: $g_x = 2.56$, $g_y = 2.56$, and $g_z = 2.33$.

Therefore, the closeness of the calculated g factors for the Nd^{3+} ions to the factor $g \approx 2.0$–2.2 that corresponds to the observed intense EPR signal attributed to the intrinsic magnetic centers in the Y–Ba–Cu–O compound allows us to make the assumption that, in the Y–Ba–Cu–O compound, the Nd^{3+} EPR signals, like the Ce^{3+} EPR signals, are masked by the intense signal from the $Cu(1)^{2+}$ copper ions.

4. CONCLUSIONS

Thus, the impurity paramagnetic centers (Ce^{3+} and Nd^{3+} rare-earth ions specially introduced) in the $YBa_2Cu_3O_{6.13}$ polycrystalline compound were investigated by the EPR method. The EPR spectra of Ce^{3+} and Nd^{3+} impurity ions in unoriented powders of the this compound were observed and interpreted for the first time. Since the components of the g factor of the Ce^{3+} and Nd^{3+} ions are close to 2, the Ce^{3+} and Nd^{3+} EPR signals cannot be separated in these compounds beginning with some instant of time when the intensity of the signal at $g \approx 2$ increases drastically.

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